

CHARACTERIZATION OF TRANSPARENT AND CONDUCTING DOPED TITANIUM DIOXIDE FOR ENERGY CONVERSION

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ABSTRACT

Niobium-Doped Titanium Dioxide thin films were prepared by RF magnetron sputtering at room temperature. The TiO₂ thin films were deposited with thicknesses of about 400 nm, doped with different concentration of niobium and then annealed in H₂ environment at 460°C. The influence of doping and post deposition annealing in H₂ environment on the structural and composition was studied by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The structure and composition of the prepared films were found to be affected by the Nb dopant concentration and the post deposition annealing. This study found that doping TiO₂ with Nb implying improved conductivity compared to pure TiO₂ which exhibits insulating properties. TiO₂/p-CdTe photovoltaic devices with efficiency of about 2 % were fabricated.

Keywords: titanium dioxide, niobium doping, XRD, XPS, photovoltaic device

INTRODUCTION

Titanium dioxide is widely used in a range of applications such as sensing, photocatalyst, antimicrobial coatings, air purification, water treatment, dye-sensitized solar cells (DSSCs), etc. For the practical applications anatase and rutile structures are widely used and are easier synthesized in thin film form. Metal-doping was the dominant way at the initial stage of the study about doping effect on the photocatalytic properties of TiO₂. It was reported that the introduction of metal ions into the TiO₂ matrix could significantly influence photoactivity, charge carrier recombination rates, and interfacial electron-transfer rates.

METHOD

Fabrication of nanostructured Nb doped TiO₂ thin films

TiO₂ thin films were prepared on glass substrates by RF magnetron sputtering of Ti target of 99.99% purity. To obtain doped films, sintered pellets made of Nb₂O₅ powder (99.999% purity) were placed on the titanium target in the circular high-intensity sputter track region. The sputtering was performed under a mixture of 5 sccm (standard cubic centimeters per minute) of Ar (99.99%) and 1 sccm of O₂ (99.99%) atmosphere supplied as working and reactive gases, respectively, through an independent mass-flow controller. The sputtering chamber was evacuated down to 1×10^{-5} mbar by the turbo molecular pump and the working pressure was kept at about 5×10^{-3} mbar. The distance between the target and the substrate was kept constant at 6 cm. Before the deposition, the glass substrates were sequentially cleaned in an ultrasonic bath with acetone and ethanol. Finally, the substrates were rinsed with distilled

water and dried. After the deposition, undoped and Nb-doped TiO₂ films were annealed in hydrogen environment. This paper reports the effect of niobium doping on structural and composition of TiO₂ prepared by RF magnetron sputtering and also, discuss the influence of annealing in H₂ atmosphere at 460°C for 30 min at a pressure of 2.0·10⁻³ mbar.

Characterization of samples

The structure of the films was investigated by X-ray diffraction (XRD) using a Bruker-AXS D8 Advance diffractometer (CuK_α radiation, 40 mA, 40 kV). The surface morphology was investigated using an NT-MDT Solver Pro-M atomic force microscope operated in tapping mode. X-ray Photoelectron Spectroscopy measurements, using a Physical Electronics PHI 5000 VersaProbe instrument, were carried out to determine the surface elemental composition of the samples and the oxidation state of the elements. The photovoltaic characteristics of solar cells were evaluated from the current–voltage characteristics, under 100 mW/cm² illumination, by means of a Spectra Physics Oriel 300W Solar Simulator.

RESULTS AND DISCUSSION

Effect of Nb doping on the structure and composition of TiO₂ thin films

Figure 1 illustrates diffraction pattern of TiO₂ thin films with different atomic concentrations of Nb. The diffraction peaks of Nb doped TiO₂ thin films shift towards lower diffraction angles with increased dopant concentration. The shift of diffraction angles indicates increase in the lattice parameters with increasing Nb doping according to well know Bragg's Law equation. With further increasing of the Nb concentration X-ray diffraction patterns show that the films are amorphous.

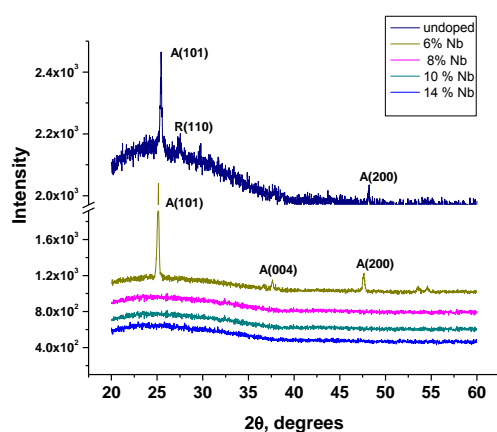


Table 1 Structural parameters of TiO₂ thin films

	a, Å	c, Å
undoped	3.7842	9.5185
6 at. % Nb	3.8214	9.5868

Fig. 1 XRD patterns of the undoped and Nb-doped TiO₂ thin films

Table 1 indicates noticeable increase of the lattice parameters with increasing of Nb concentration. No characteristic peaks of Nb₂O₅ were observed in Nb-doped TiO₂ thin films. The survey XPS spectra of the Nb doped TiO₂ films in the whole binding energy region showed in the first atomic layers (10 nm) the characteristic peaks of C1s, O1s, Nb3d and Ti2p. Fig. 2 and Fig. 3 show the high-resolution Nb3d doublet and Ti2p doublet regions of TiO₂ films with different Nb dopant concentrations. As one can see Nb3d peak intensity increases with increasing concentration of Nb, while the Ti2p peak intensity decreases. Also, a slight shift to higher binding energy with increasing Nb content in XPS spectra of Nb3d

region is observed. Development of photovoltaic devices with higher efficiency requires nanostructured conductive materials. Therefore further we studied the effect of annealing in H_2 environment on the Nb-doped TiO_2 nanocrystalline structure.

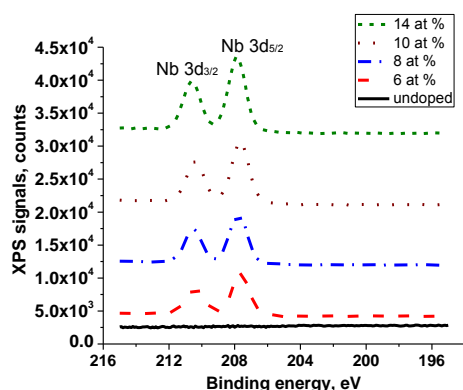


Fig. 2 XPS spectra of Nb3d region of TiO_2 with different Nb concentration

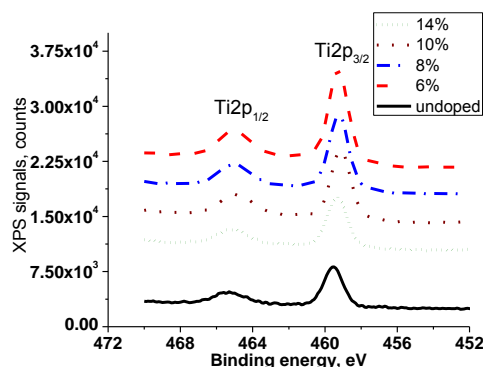


Fig. 3 XPS spectra of Ti2p region of TiO_2 with different Nb concentration

Effect of annealing in hydrogen atmosphere on the structure and composition

The diffraction pattern of the undoped, 6 at. % Nb-doped TiO_2 film and 6 at. % Nb-doped TiO_2 film annealed in H_2 environment at $460^\circ C$, 30 min is shown in Fig. 4. The various diffraction peaks could be assigned to reflections corresponding to the anatase and rutile phases of TiO_2 for the undoped. The weight percentage of the anatase phase is 59.3%.

The 6 at.% Nb-doped TiO_2 films and 6 at. % Nb-doped TiO_2 films annealed in H_2 environment at $460^\circ C$, 30 min TiO_2 films exhibit only the anatase phase. Also, the XRD data show that the crystallinity is improved when the films are doped. Annealing at $460^\circ C$ in H_2 atmosphere results in an increase in the intensity of the diffraction peak located at $2\theta = 25.2^\circ$ and it is found that the peak position of (101) anatase plane shifts to smaller diffraction angle value. We suppose that the primary hydrogen annealing mechanism is the chemisorptions of the dissociated hydrogen on the surface of the films. The half width of all the peaks of the Nb-doped and annealed TiO_2 thin films increases. The crystallite size was calculated by Scherrer equation using anatase (101) phase. For comparison the crystallite size increases from 47 nm for not annealed Nb-doped TiO_2 film to 55 nm for Nb-doped annealed in H_2 atmosphere at $460^\circ C$.

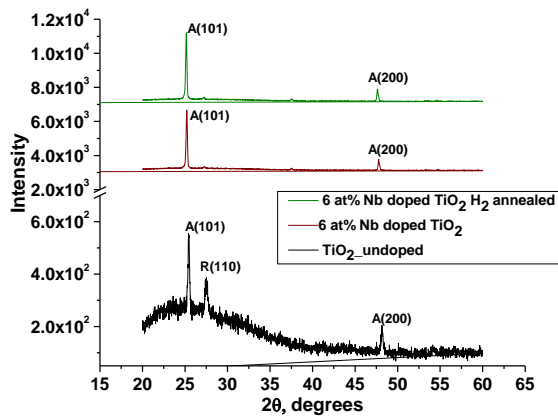


Fig. 4 XRD patterns of the TiO_2 thin films

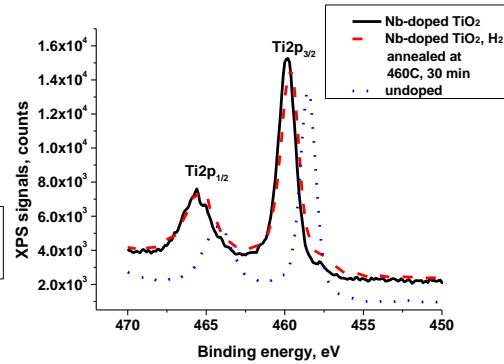


Fig. 5 XPS spectra of $\text{Ti}2p$ region of TiO_2 thin films

Fig. 5 shows the high-resolution $\text{Ti}2p$ doublet of the undoped TiO_2 films, 6 at.% Nb-doped and 6 at.% Nb-doped annealed in H_2 environment at 460°C , 30 min. For the undoped TiO_2 film the spectrum indicates binding energies at 458.5 ± 0.2 eV for $\text{Ti}2p_{3/2}$ and 464.3 ± 0.2 eV for $\text{Ti}2p_{1/2}$, respectively, which are very close to the values of the Ti^{4+} valence state of stoichiometric rutile TiO_2 [1, 2]. The $\text{Ti}2p$ XPS spectra of 6 at.% Nb-doped TiO_2 films show values of binding energies of 459.7 ± 0.2 eV for $\text{Ti}2p_{3/2}$ and 464.9 ± 0.2 eV for $\text{Ti}2p_{1/2}$, respectively. For the film doped and annealed in H_2 atmosphere, a slight shift (~ 0.2 eV) towards higher BE values is seen for $\text{Ti} 2p_{3/2}$ and (~ 0.6 eV) for $\text{Ti} 2p_{1/2}$. The position of the $\text{Ti} 2p_{3/2}$ peak (458.8 eV) is close to the value reported for Ti^{3+} states in the anatase phase (458.7 eV) [3]. We believe that the H_2 annealing changes the $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratio in the TiO_2 thin film. Both $\text{Ti}2p_{1/2}$ and $\text{Ti}2p_{3/2}$ binding energies showed a change in Ti^{3+} states and the Ti^{4+} ions, as a consequence of the H_2 treatment. A chemical shift of the BE is known to mean changes in the structure. Since the ionic radius of Nb^{5+} (0.70 \AA) is larger than the ionic radius (0.68 \AA) of the titanium, we can thus conclude that the Nb is easily built into a lattice, adding electrons. The theoretical calculations of Morgan [4] predict a small-polaronic Ti^{3+} gap state within an Nb-doped TiO_2 thin film. For Nb dopant at this concentration, the defect can be characterized as Nb^{5+} and $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratio. The XPS spectra of the Nb3d region of 6 at.% Nb doped TiO_2 and of 6 at.% Nb doped TiO_2 and annealed in H_2 environment at 460°C , 30 min are illustrated in Fig.6. The peaks correspond to that of Nb^{5+} oxidation state [5, 6]. The Nb3d binding energy for the 6 at.% Nb-doped TiO_2 film was determined to be 208.2 ± 0.2 eV for Nb $3d_{5/2}$ and 211.0 ± 0.2 eV for Nb $3d_{3/2}$, while for the annealed in hydrogen, the BE values are 207.9 ± 0.2 eV and 210.8 ± 0.2 eV, respectively. We suppose that observed slight shift is caused by the effect of annealing in H_2 atmosphere. To maintain the charge equilibrium, the extra-positive charge due to Nb^{5+} may be compensated by the creation of an equivalent amount of Ti^{3+} ions [7] or by the presence of vacancies in the cation sites [8]. Nb^{5+} species, substituting for Ti^{4+} in the crystalline lattice could be a reason for anatase stabilization.

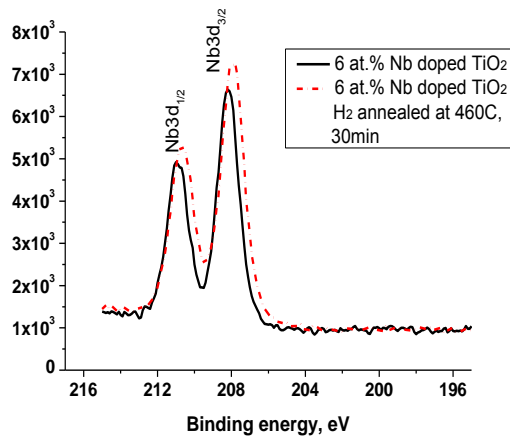


Fig.6 XPS spectra of Nb3d region of TiO₂ thin films

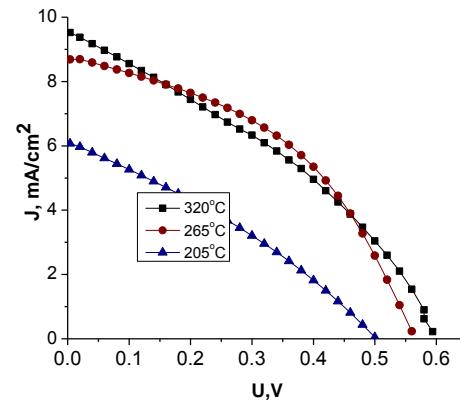


Fig.7 J-V characteristics of the TiO₂/CdTe photovoltaic devices under 100 mW/cm² illumination, 300 K.

Characterization of the TiO₂/p-CdTe photovoltaic devices

The 6 at.% Nb-doped TiO₂ films annealed in H₂ environment at 460°C has been applied in the fabrication of the photovoltaic devices. The load current-voltage characteristics of the TiO₂/pCdTe photovoltaic devices under illumination 100 mW/cm² are shown in Figure 7. The photovoltaic parameters depend on the shape of the J-U curve which is influenced by the substrate temperature of the CdTe thin films. An inspection of Table 2 where are presented the photovoltaic parameters shows that the efficiency of the devices is low because of the low values of the open circuit voltage and the fill factor. Poor efficiency of these devices could be attributed first to the higher sheet resistance of TiO₂ films and secondly to the relatively high concentration of mismatch dislocations at the TiO₂/CdTe heterojunction interface.

Table 2 Photovoltaic parameters of TiO₂/CdTe photovoltaic devices

$T_s, ^\circ\text{C}$,	J_{sc} , mA/cm ²	U_{oc} , V	FF	η , %
225	6.1	0.51	0.27	0.85
298	9.12	0.43	0.42	1.63
320	9.5	0.59	0.36	1.98

CONCLUSION

Annealing in hydrogen atmosphere showed substantial improvement of structural properties of Nb-doped TiO₂ thin films. The Nb ions incorporate into the TiO₂ lattice. The XPS results indicate that the charge transfer from Nb metal ions to Ti leads to a change in the oxidation state of titanium. The H₂ annealing changes the Ti³⁺/Ti⁴⁺ ratio in the TiO₂ thin film. The highest efficiency achieved at TiO₂/CdTe photovoltaic devices is about 2%.

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